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Process for cleaning articles

[0001]

Technical Field

This invention relates to methods for cleaning articles and materials made of metal, glass, ceramics, plastics, or composites thereof or textiles.

[0002]

Description of the Related Art

Cleaning processes in which a vapor produced by heating of an active cleaning liquid is brought into contact with articles to be cleaned are employed in the cleaning of a very wide variety of articles, such as metal articles, industrially manufactured articles such as circuit boards, articles of clothing, etc, to remove undesirable foreign substances such as fats, lapping and polishing pastes, soldering pastes, adhesives, mixtures of inorganic (e.g., saline) fouling substances and organic fouling substances (e.g., ones consisting of fatty residues), etc. Until recently chlorinated hydrocarbons were typically used for such cleaning tasks. But now, because of their inadequate environmental compatibility, and especially due to their ozone destruction potential, their carcinogenicity, and their toxic effect, chlorinated hydrocarbons have been banned or use is allowed only under very strictly defined conditions. One advantage of using chlorinated hydrocarbons was that such substances do not have a flash point. Because of these disadvantages, chlorinated hydrocarbons have been replaced by other hydrocarbons or solvents such as polypropyleneglycol ether, alcohols, acetone, and the like. The latter have flash points in the range of normally occurring temperatures and are consequently ignition hazards. They also present another disadvantage in that these solvents hardly remove pigment fouling or fouling caused by ionic salts, since these solvents are very inefficient in dissolving pigments or salts due to the ionic nature of the latter.

[0003]

SUMMARY OF THE INVENTION

The object of the invention was to develop a generic cleaning process so that a good cleaning effect may be achieved in an environmentally compatible manner.

[0004]

Another object of the invention was to prepare a new cleaning process whereby mixtures of inorganic and organic fouling may be removed simultaneously in an efficient manner. An additional object of the invention includes preparation of methods for cleaning metal articles and materials, which methods are not as harsh in the results of operation as are state-of-the-art processes.

[0005]

The objects referred to above are attained by one or more of the methods disclosed herein.

[0006]

Azeotropic preparations disclosed herein, which are usable as active cleaning liquids, provide the advantage above all that, due to the aqueous component, the liquid phase efficiently dissolves pigment fouling and fouling with ionic components such as salts, if the azeotropic preparation used as the active cleaning liquid contacts the articles. By including at least one compound containing lipophilic groups, which compound preferably also is a liquid under ambient conditions or at low treatment temperatures, the azeotropic preparation will possess efficient lipolytic capability.

[0007]

If the azeotropic preparation used as the active cleaning liquid is heated, because of its azeotropic nature (for a definition of "azeotrope" see Römpps Chemie Lexikon [Römpps's Chemical Dictionary], 9th Edition (1989), page 323), both water and the other component(s) pass(es) into the vapor phase in a composition corresponding to that of the specific azeotrope. When the vapor of the azeotropic preparation contacts the articles to be cleaned, reliable

cleaning and "rinsing" from the articles of the fouling substances removed by the cleaning process is effected.

[0008]

It is particularly advantageous that the vapor, because of its high water content, is not combustible. Precautionary measures in this connection are not required in a device used for application of the present methods. The flash point of the vapor, to the extent that such exists, is higher than the temperatures normally occurring in such a cleaning process, but at least above the boiling point of the liquid and preferably above about 200 °C. A flash point above 200 °C is especially preferable in that the precautionary measures taken while performing the cleaning process are less extensive than when active cleaning liquids with lower flash points are used. The azeotropic preparation present in at least one part of the present methods may be condensed to the liquid phase either on the articles to be cleaned or by lowering of the temperature, so that costly measures to protect the atmosphere surrounding the device utilized to perform the method, such as are required in conventional processes, may be eliminated to the greatest possible extent.

[0009]

Hence an additional advantage of the present methods is the fact that very little of the azeotropic preparation employed as the active cleaning liquid is used, because the liquid is recondensed to the greatest extent possible. A closed loop may thus be created in which the azeotropic preparation used as active cleaning fluid need not be replenished or only in negligibly small amounts. An additional contribution to this result is made by the fact that the present azeotropic preparations utilized as active cleaning liquids may be free of surfactants, which surfactants are deposited on the filter surface during filtration of the active cleaning liquid in conventional processes for precipitation of fouling substances and require reinforcement in conventionally used solutions.

[0010]

Surprisingly, the present methods may also be used to remove complex types of fouling substances, such as dried body fluids or other fouling substances occurring in everyday life as a result of precipitation in the form of rain or snow, etc, from articles to be cleaned.

[0011]

The present methods are not limited to closed systems. The present methods may, for example, also be utilized in the form of open jet steam cleaning.

Figure 1 illustrates a representative device for performing cleaning processes according to the present teachings.

[0012]

Detailed Description of the Invention

In selection of the present azeotropic preparations used as the active cleaning liquid or of the other component(s) that the preparations contain, which preparations contain molecules having hydrophilic groups (e.g., -OH, -NH₂, -C-O-C-, C(=O)-C-, -C(=O)-O, etc) and lipophilic groups (e.g., CH₂ chains or C₁ to C₁₂, etc), emphasis is placed on the following criteria, in addition to good cleaning power. The moisture content of the azeotrope comprising water and at least one other compound must be high enough so that there is no flash point, that is, so that the vapor is not combustible. The liquid and the vapor formed by heating the liquid must neither be toxic nor have ozone destruction potential, nor may the liquid present a water hazard if the preparation is inadvertently released into the environment. Water soluble components forming homogeneous azeotropes or water insoluble components forming heterogenous azeotropes are suitable.

[0013]

A preferred process for cleaning articles comprises steps in which:

- an azeotropic preparation is formed of water and at least one compound having hydrophilic and lipophilic groups in a weight ratio (compounds having hydrophilic and lipophilic groups to water) of 0.05 to 99.5 : 99.95 to 0.05;

- the articles to be cleaned are brought at least once into contact with the azeotropic preparation and then the liquid azeotropic preparation, including the foreign substances removed with it, is drained from the articles to be cleaned;

- residues of the azeotropic preparation on or in the articles to be cleaned are removed by evaporation; and

-the vapor of the azeotropic preparation is condensed and the azeotropic preparation recovered by condensation is used for a repeated cleaning step.

[0014]

The foregoing corresponds to an especially preferred embodiment of the present methods, one in which articles to be cleaned are brought at least once into contact with the vapor of the azeotropic preparation and the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned. For example, the articles may be brought into contact with the liquid azeotropic preparation only once or several times, for example, by immersion, spraying, sprinkling or the like, using processes in the state-of-the-art already known for application of a liquid. The articles may subsequently be brought one or more times into contact with the vapor of azeotropic preparation. The vapor of the azeotropic preparation normally condenses on the articles and carries with it residues of foreign substances from the cleaned articles as it drains. As an alternative, however, the present methods may be applied by bringing articles to be cleaned immediately into contact with a vapor of the azeotropic preparation, at least once but preferably several times. In this instance as well, the vapor condenses while contacting the articles and removes the fouling substances.

[0015]

In an especially preferred embodiment of the present methods, use is made of an azeotropic preparation of water and at least one compound having hydrophilic and lipophilic groups, in which the weight ratio of the compound(s) having hydrophilic and lipophilic groups to water is in the range of 1.0 to 35.0 : 99.0 to 65.0, and even more preferably in the range of 4.0 to 15.0 : 96.0 to 85.0.

[0016]

Corresponding to another preferred embodiment is use of an azeotropic preparation in the form of a mixture of water and at least one additional compound having hydrophilic and lipophilic groups as the active cleaning liquid, in which the additional compound and the water form an azeotrope in the liquid-phase-to-vapor-phase transition and the azeotrope has an immiscibility gap at a temperature ranging from 0 °C to the temperature of the phase liquid-phase-to-vapor-phase transition under normal pressure. Surprisingly, it has been found that azeotropes having immiscibility gaps possess particularly advantageous cleaning

properties. Particular preference is to be given to an azeotrope having an immiscibility gap at a temperature ranging from 20 °C to 110 °C under normal pressure.

[0017]

The term "under normal pressure" is intended herein to mean atmospheric pressure (approximately 1 or about 10^5 Pa).

[0018]

While at this point no theoretical interpretation has been deduced for the invention, it has been found that azeotropic preparations, which may be used as an active cleaning liquid in the present methods, are clear at low temperatures ranging, for example, from 20 to 25 °C. In other words, the components are fully dissolved in each other. Specific component composition relationships are established at each temperature in the mixed phase. The phases which are separate at high temperatures can be converted to an emulsion that is milky in appearance by means of suitable process steps, such as preferably treatment with ultrasound, intensive movement during transfer by pumping or agitation, etc. This emulsion exhibits droplets of the organic component(s) in a continuous aqueous phase. The emulsion possesses excellent fat dissolving capability due to the content of organic components (i.e., molecules having lipophilic groups); in addition, the continuous aqueous phase also dissolves water-soluble, e.g., ionic, fouling substances, such as salts. When the temperature of an azeotropic preparation is further raised, the preparation passes into the vapor phase, in which the components are present in the specific composition typical of the particular azeotrope. During condensation the azeotropic preparation again migrates through the immiscibility gap; consequently, condensing vapor of the azeotropic preparation is present again on the articles to be cleaned, in the form of the emulsion, which possesses excellent dissolving properties both for lipid and for ionic fouling substances.

[0019]

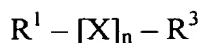
In the light of the criteria indicated above, some organic components which form homogenous azeotropes with water are given preference for use as organic components in azeotropic preparations employed for application of the present methods.

[0020]

As may readily be discerned by experts in this area of the art, the invention is nevertheless not limited to the preferred compounds forming azeotropes.

[0021]

The preferred compounds can best be described by the following general formula:



wherein

- R^1 and R^3 each represent H independently of each other; straight-chain or branched unsaturated C_1 - to C_{18} - alkyl groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; saturated or unsaturated cyclic C_1 - to C_8 - alkyl groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; hydroxy; C_1 - to C_8 - alkoxy; amino, wherein one or both hydrogen group(s) may be replaced by C_1 - to C_8 - alkyl groups; and

- X represents $-O-$, $-C(=O)-$; $-C(=O)-O-$; NH ; $-NR^1-$; $-N(-OH)-$; straight-chain or branched - (C_1 - to C_8 -) alkylene groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; and n represents integers 1, 2, 3, etc.

[0022]

In other words, the organic components of the azeotropic preparations, which may be used in the present methods, may be selected from among organic compounds belonging to the groups of alcohols, glycols, amines, ethers, glycol ethers, esters, ketones, and amino alcohols and from among N-heterocyclene or organic acids.

[0023]

In especially preferred methods, compounds having the general formula indicated above are used as an organic component or components of the azeotropic preparation or as an additional organic component or components, in which R^1 and R^3 each independently

represents saturated C₁- to C₁₂- alkyl groups, and with even greater preference saturated or unsaturated C₁- to C₈- alkyl groups in which one or more nonadjacent CH₂ group(s) may be replaced by -O-; may represent hydroxy, C₁- to C₈- alkoxy and unsubstituted or alkyl group substituted amino groups; and/or X represents -O-; -C(=O)-; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)=; -OCH(R²)-CH₂- (where R₂ represents H or methyl); and n represents 1 or 2.

[0024]

Specific examples of groups represented by R¹ and R³ are hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, furfuryl-2, tetrahydrofurfuryl-2, hydroxy, methoxy, ethoxy, and propoxy. Specific examples of the groups represented by X are -O-; -C(=O)-; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)-; ethyleneoxy; and propyleneoxy.

[0025]

Even more preferred methods employ compounds of the general formula indicated above as an organic compound or compounds of the azeotropic preparations or as an additional organic component or components which are selected from among those in the group:

- (C₁- to C₁₂- Alkyl) - C(=O)-O - (C₁- to C₁₂- Alkyl);
- (C₁- to C₁₂- Alkyl) - O - (C₁- to C₁₂- Alkyl);
- (C₁- to C₁₂- Alkyl) - C(=O) - (C₁- to C₁₂- Alkyl);
- (C₁- to C₁₂- Alkyl) - [N- (H or C₁- to C₁₂- Alkyl) (H or C₁- to C₁₂- Alkyl)];
- HO-(CH₂)_{1, 2 ... etc.} - [NH₂ or NH(C₁- to C₁₂- Alkyl) or N(C₁- to C₁₂- Alkyl)₂];
- H - [O - CH(H or CH₃) - CH₂]_{1, 2 ... etc} - OH; and
- (H or C₁- to C₁₂- Alkyl) - [O -CH(H or CH₃) - CH₂]_{1, 2 ... etc.} - [OH or O(C₁- to C₁₂- Alkyl)].

[0026]

Specific examples of organic compounds which may be used, either singly or together in groups of a plurality of the compounds named in azeotropic preparations of the active

cleaning liquid, are selected from the group comprising propyleneglycol ether; dipropyleneglycolmonoethylether; tripropyleneglycolmonomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl-)pyridine; ethanolamine; furfurylamine; methyl lactate; isopropyl lactate; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0027]

Addition to the active cleaning liquid for the present methods of at least one cleaning booster, which does not spontaneously evaporate, corresponds to another especially preferred embodiment. It or they should preferably be distilled with the azeotropic preparation. Such cleaning boosters which do not spontaneously evaporate are known to the expert from the state of the art and require no further specification at this point.

[0028]

Preferably, at least one corrosion inhibiting additive is added to the active cleaning liquid. Such additive or additives should preferably be distilled with the azeotropic preparation. Such corrosion inhibiting additives are particularly advantageous when articles made of nonferrous heavy metals or light metals will be cleaned. For example, excellent cleaning of aluminum articles can be accomplished using an azeotropic preparation comprising 1-methylimidazole, which acts as an inhibitor. Copper parts may also be advantageously cleaned using azeotropic preparations comprising 1-methylimidazole. Brightening of the surface is achieved by the process. In place of the indicated compound, use may also be made of other corrosion inhibiting additives and inhibitors known to the expert from the state of the art.

[0029]

Especially preferred as yielding excellent cleaning results are processes for cleaning articles, in which an azeotropic preparation of water and an organic component is added as active cleaning liquid. By preference the organic component is in this instance a compound selected from among those in the group comprising dipropyleneglycolmonomethylether; dipropyleneglycolmono-n-propylether; tripropyleneglycol monomethylether; 3-methoxy-3-

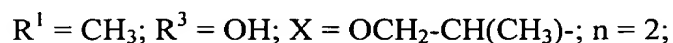
methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; furfuryl amine; methyl lactate and isopropyl lactate.

[0030]

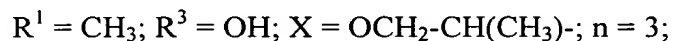
The below-identified compounds belong to the following groups of compounds having the general formula $R^1 - [X]_n - R^3$:

(A) Glycol ethers:

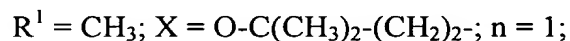
-organic component No. 1: dipropyleneglycolmonomethylether



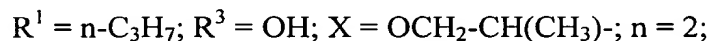
-organic component No. 2: tripropyleneglycolmonomethylether



-organic component No. 3: 3-methoxy-3-methylbutanol

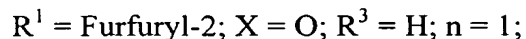


-organic component No. 4: dipropyleneglycol-n-propylether

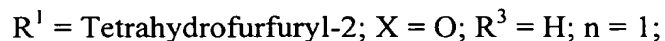


(B) Alcohols:

-organic component No. 5: furfuryl alcohol



-organic component No. 5: tetrahydrofurfuryl alcohol



(C) Amines:

-organic component No. 7: 1-aminobutanol-2



-organic component No. 8: furfurylamine

$R^1 = \text{Furfuryl-2}; X = -\text{NH-}; R^3 = \text{H}; n = 1;$

-organic component No. 11: 2-amino-2-methylpropanol-1

$R^1 = \text{CH}_3; X = \text{CH}_3 - \text{C} - \text{CH}_2\text{OH}; R^3 = -\text{NH}_2; n = 1;$

-organic component No. 12: 2-amino-2-methylpropanediol-1,3

$R^1 = \text{HOCH}_2; X = \text{CH}_3 - \text{C} - \text{CH}_2\text{OH}; R^3 = -\text{NH}_2; n = 1;$

(D) Esters:

-organic component No. 9: methyl lactate

$R^1 = \text{Hydroxyethyl}; X = \text{C}(=\text{O})\text{O-}; R^3 = \text{CH}_3; n = 1; \text{ and}$

-organic component No. 10: isopropyl lactate

$R^1 = \text{Hydroxyethyl}; X = \text{C}(=\text{O})\text{O-}; R^3 = i\text{-C}_3\text{H}_7; n = 1.$

[0031]

In the present azeotropic preparations, water and an organic component are added in the relative amounts of $(100 - x)$ percent by weight : x percent by weight. In this statement x ranges from $0 < x \leq 35$, is preferably in the range $3 \leq x \leq 25$, and by special preference is in the range $4 \leq x \leq 15$.

[0032]

In another preferred process the mixture ratio of water to the other component(s) in the azeotropic preparation is set more or less at the ratio which is present in the vapor as a result of heating of the liquid azeotropic preparation.

[0033]

In another, also preferred, embodiment, the process for cleaning articles includes a step in which an azeotropic preparation containing water and two organic components is used as the active cleaning liquid. By particular preference, use is made of an active cleaning liquid containing an azeotropic preparation consisting of water, dipropyleneglycolmono-n-propylether and an additional organic component. The azeotropic preparation employed as active cleaning liquid may, of course, also contain other components, such as at least one

cleaning booster that does not spontaneously evaporate and by special preference is distilled with the azeotropic preparation, a cleaning booster such as is known from the state of the art and has been referred to in the foregoing, and/or at least one corrosion inhibiting additive or corrosion inhibitor (by special preference one distilled with the azeotropic preparation) such as is also known as such or is known from the state of the art and has already been referred to in the foregoing.

[0034]

In accordance with this preferred embodiment, by special preference, use is made of an additional organic compound selected from the group: 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl)-pyridine; ethanolamine; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0035]

The organic compounds indicated above may be used singly or in combination with each other.

[0036]

Also to be given particular preference is use of an additional organic component selected from the group made up of acetic acid, hydroxy acetic acid, formic acid, and butyric acid. The acids in question may also be used individually or in combination with each other or with other substances, such as the organic components named above.

[0037]

In accordance with the preferred embodiment just described, use is made of an active cleaning liquid containing an azeotropic preparation consisting of water, a glycol ether (preferably dipropyleneglycolmono-n-propylether) and an additional organic component in the relative amounts of 90 percent by weight : (10 - y) percent by weight : y percent by weight, where y is in the range $0 < y \leq 5$, and by special preference $0 < y \leq 2$.

[0038]

Figure 1 shows a schematic drawing of a device that may be utilized to perform the present methods, which device includes: a storage tank 2 with a separation compartment 4 and an overflow compartment 6 that is connected via a feed pump 8 and a heating device 10 to a cleaning device 12. The interior of the cleaning device 12, whose structure is of the state of the art and which may include cleaning nozzles, a revolving basket, etc, is connected to a pressure compensation vessel 14, as shown in Figure 1. However, the pressure compensation vessel 14 is not essential for operation.

[0039]

Piping leads from the bottom of the cleaning device 12 to a filter device 16. The filter device 16 is connected via piping to a feed pump 18 on the top of the separation compartment 4. Additional piping extends from the filter device 16 via a vacuum pump 20 through a condenser 22 and a cooler 24 back to the separation compartment 4.

[0040]

Piping also extends from the overflow compartment 6 via a delivery pump 26 through a heat exchanger 28 into a distillation device 30 and thence back into the cleaning device 12 or back to the storage tank 2.

[0041]

A feed line 32 for charging the storage tank 2 with active cleaning liquid extends into the storage tank 2. The storage tank 2 also contains a device, not shown, for removal of sludge deposited in the separation compartment 4.

[0042]

Ventilation piping 34 extends into the normally sealed cleaning device 12.

[0043]

The structure of the individual structural elements of the cleaning device 12 and an electric control unit (not shown) for the individual structural components is of the state of the art and is consequently not described in detail.

[0044]

The above-described device operates as follows. After the cleaning device 12 has been charged with an article or articles to be cleaned, in an exemplary but not restrictive embodiment, the feed pump 8 is actuated and active cleaning liquid, whose temperature may if desired be adjusted in the heating device 10, is fed to the cleaning device 12. In the cleaning device 12 the revolving article or articles to be cleaned is/are immersed and/or the article or articles to be cleaned are sprayed with liquid. The liquid is removed from the cleaning device 12 through the filter device 16 by the feed pump 18 and is fed into the separation compartment 4. Predominantly inorganic fouling substances are precipitated in the filter device 16 and are removed. Predominantly fatty fouling substances are precipitated in the separation compartment 4 and are also removed.

[0045]

The liquid cleaning stage described as an example is followed by rinsing under the same conditions with active cleaning liquid from the tank 6.

[0046]

The rinsing is followed by a steam cleaning or steam rinsing stage in which the feed pump 26 is actuated and then the active cleaning liquid is heated in the distillation device and converted into vapor. Because of the azeotropic nature of the azeotropic preparation employed as the active cleaning liquid, this vapor has a predetermined content of water and the additional component or components. The composition of the liquid azeotropic preparation is preferably such that it corresponds in point of content to the components in the vapor phase. In the cleaning device 12 the vapor comes into vigorous contact with the article or articles to be cleaned; at least a part of the vapor is condensed. The feed pump 18 delivers the condensate to the precipitation compartment after this condensate has passed through the filter device 16.

[0047]

The liquid may be reconditioned if the vapor is fed back into the storage tank 6 from the distillation device 30 via the condenser 22 and the cooler 14.

[0048]

The vapor cleaning or vapor rinsing is advantageously followed by circulating air drying or vacuum drying. In the process the vapor present in the cleaning device 12 is drawn off by the vacuum pump 20, and the condensate formed in the cleaning device 12 passes through the filter device 16. The vapor mixed with the condensate is returned to the storage tank 2 as liquid after passing through the condenser 22 and cooler 24.

[0049]

After vacuum drying has been completed, the separation compartment 4 is aerated by the aeration line 34, and the cleaned article(s) may be removed.

[0050]

In an alternative embodiment, which also yields favorable results, articles to be treated are sprayed in the cleaning device 12 with the azeotropic preparation used as the active cleaning liquid. In this process articles to be cleaned are soaked in the liquid. The subsequent process steps are more or less the same as those described in the foregoing.

[0051]

After treatment the cleaned articles are in a distinctly better condition than after treatment using a conventional process, that is, by use of conventional organic solvents for the cleaning steps under identical conditions. In particular it has been found, surprisingly, that all inorganic fouling substances, in particular inorganic salts from perspiration, coloring pigments, etc, are removed in addition to all organic fouling substances such as lipophilic or oleaginous or fatty substances. The cleaned articles do not have an unpleasant odor and are outstanding in appearance.

[0052]

As was stated above, azeotropic preparations having an immiscibility gap exhibit a surprisingly efficient cleaning behaviour that is distinctly superior to conventional preparations.

[0053]

Whenever use is made of azeotropic preparations having an immiscibility gap, during treatment in the liquid phase, articles to be cleaned are brought into contact with an azeotropic preparation which is in a state such that the components of the azeotropic preparation are present in separate, or at least partly separate, phases. For example, liquid azeotropic preparations in a state of phase separation are treated with ultrasound or are vigorously transferred by pumping or agitated so that a milky emulsion of the azeotropic preparation is formed. This emulsion efficiently dissolves not only fatty or oily components but ionic or saline fouling substances as well.

[0054]

Whenever articles to be cleaned are treated with the azeotropic preparation in the vapor phase, as described above the azeotropic preparation is heated and a vapor is produced in which the components are present in the quantitative proportions determined by the characteristic azeotropic properties. The vapor condenses at least to some extent on the articles to be cleaned, and the same milky emulsion is obtained as in the liquid phase. Efficient dissolving of fats and salts is observed in this instance as well.

[0055]

When the temperature of the azeotropic preparation is raised to the point of the liquid phase/vapor phase transition, the components pass into the vapor phase in the quantitative proportion corresponding to that of the azeotrope, and the azeotropic preparation can be produced by distillation without any problem.

[0056]

The last-named embodiment is particularly favorable for cleaning metal parts. Thus, for example, lapping and polishing pastes can be very efficiently removed from metal parts by using azeotropes having an immiscibility gap. For instance, an azeotropic preparation that includes acid additives is used as the active cleaning liquid for this purpose. Cleaning is performed in the one-compartment system described above and may be continuously performed or in a batch process.

[0057]

SMD adhesives (SMD = surface mounted devices), which are utilized during the manufacture of SMD components, can also be removed surprisingly well from electronic components produced in double-sided assembly so as to prevent components from being detached during the soldering process. The adhesive is typically applied by dispenser systems or templates before the printed circuit boards are secured. Defectively printed or dispensed circuit boards or templates may be cleaned. Surprisingly, cleaning results distinctly superior to those results obtained with conventional solvents, such as butyl acetate or isopropanol, can be obtained with the present azeotropic preparations. In addition, precautionary safety measures (such as those measures taken to prevent explosions when hazardous solvents are used) are not necessary.

[0058]

The above-identified azeotropic preparations may be used similarly in the present methods in order to remove excess soldering paste applied while soldering in a simple and environmentally friendly manner from defectively printed circuit boards and templates. It is also possible to remove excess fluxing agent residues after soldering. Cleaning is accomplished by spraying, spray rinsing, and drying of articles to be cleaned, preferably in an immersion process involving ultrasound (cleaning stage), rinsing with or without ultrasound (rinsing stage), and drying. Cleaning is preferably performed at a temperature in the range of 40-60 °C, but is not restricted to this temperature range. The temperature may be significantly higher; for example, the temperature may even exceed 100 °C, especially during treatment of articles to be cleaned during the cleaning stage using the vapor of the azeotropic preparation.

[0059]

Particular preference is given to use of the azeotropic preparations presented in Table I below for the present cleaning methods. Also given in this table are the preferred proportions of organic components (O.K.) to water, the boiling points of the particular azeotropic preparations, and the temperatures at which exemplary treatment of articles to be cleaned may be performed. The invention is not, of course, restricted to the proportions of the components and the treatment temperatures that are indicated in Table I.

[0060]

When azeotropes having an immiscibility gap are used, particular preference is given to three-component mixtures of water, dipropyleneglycolmono-n-propylether, and amine compounds or n-heterocyclic compounds or organic acids, as shown in Table II below. An exemplary but not restrictive composition of the azeotropes is as follows: water (90 percent by weight), dipropyleneglycolmono-n-propylether (10 percent by weight), y percent by weight of the compounds indicated in Table II.

Table I

[0061]

Azeotropic Preparation		Boiling Point (°C)	Treatment Temperature (°C)
Organic Components (O.K.)	O.K. to Water Ratio		
No. 1	8.9 : 91.1	99.2	60
No. 2	7.9 : 92.1	99.1	60
No. 3	11 : 89	99 – 101	65
No. 4	10 : 90	100	65
No. 5	20 : 80	98.5	65
No. 6	10.5 : 89.5	102	65
No. 7	4.7 : 95.3	102	65
No. 8	30.9 : 69.1	100	60
No. 9	20 : 80	99.5	60
No. 10	34 : 76	98	60
No. 11	5 : 95	98	65
No. 12	6.5 : 93.5	101	60

Table II

[0062]

Organic Components	y (% by weight)	Boiling Point (°C)
1-Aminobutanol-2	0.3	101
Monoisopropanolamine	0.8	100
2-Amino-2-methyl-propanol-1	1.3	102
2-Amino-2-methyl-propandiol-1,3	1.5	101
3-(Aminomethyl-)pyridine	0.16	101
Ethanolamine	0.3	104
Aminoacetaldehyd-dimethylacetal	2.4 3.4 4.2	101
4-Aminomorpholine	0.4	101
1-Methylimidazole	0.1	101
1,2-Dimethylimidazole	0.1	100 – 102
1-Vinylimidazole	0.3	101
DABCO	0.03 0.08 0.1	101 – 103
1,5-Diazabicyclo-[4.3.0]non-5-en	0.02	101 – 103
1,8-Diazabicyclo-[5.4.0]undec-7-en	0.02	101 – 103
Acetic Acid (80 %ig)	1.5	100 – 101
Hydroxyacetic acid	0.5	100 – 101
Formic Acid	1.5	100 – 101
Butyric Acid	1.2	100 - 101

[0063]

The boiling point (°C) of the azeotropic preparation made up of water, dipropyleneglycolmono-n-propylether, and the compounds indicated is also given in Table II.

[0064]

The invention is illustrated by the following examples, but is not restricted to these examples.

[0065]

Example 1

The drum of the cleaning device 12 described above was charged with material to be cleaned. The material, consisting of textiles, was in a first step treated under liquid cleaning conditions with azeotropic preparations at elevated temperatures. The azeotropic preparations and the pertinent treatment temperatures are indicated in Table I above. The material was dipped into the hot azeotropic preparation during agitation. The hot azeotropic preparation was fed in a closed loop from the drum of the cleaning device 12 through a filter device 16 and delivered to the separation compartment 4. In the filter device 16 predominantly inorganic fouling (salts) was deposited and also removed.

[0066]

The first treatment step was followed by a second treatment step also carried out under liquid treatment conditions. Fresh azeotropic preparation (see Table I for the composition; in each operation the azeotropic preparation of the second treatment step was of the same composition as that of the first step) was fed to the drum of the cleaning device at an elevated temperature. The material was delivered in a second closed loop from the drum of the cleaning device 12 to the separation compartment 4 via the filter device 16. The inorganic and organic substances were separated in the same way as in the first treatment step.

[0067]

The second treatment step was followed by a third treatment step in which the material was treated with the vapor of the particular azeotropic preparation, the composition of which was typical of the particular azeotropic preparation (see Table I). After passing

through the feed pump, the azeotropic preparation was converted to the vapor phase in a distillation device. The vapor was brought into intimate contact with the material in the drum of the cleaning device 12. Part of the vapor was condensed at the time of contact with the material. The liquid from the cleaning step following condensation was removed from the drum and, after passing through the filter device 16 for separation of the organic substances, was delivered to the separation compartment 4, where organic contaminants were separated. The vapor not already condensed in the drum of the cleaning device 12 was withdrawn from the drum, condensed, and (after optional filtration) delivered to the storage tank 2 for future use.

[0068]

After the vapor of the azeotropic preparation had been removed, the drum was evacuated, for example at 10^{-2} bar, and the remaining vapor was removed in the same way as described above. The hot treated material released the water and the organic components of the azeotropic preparation in the vacuum, with the result that the material was dry after 10 minutes of vacuum treatment.

[0069]

The treated material was in much better condition than the same material that was treated by conventional means. Both inorganic and organic fouling substances were entirely removed. The material gave off no unpleasant odor and was outstanding in appearance. It was successfully ironed or pressed.

[0070]

The third step (vapor treatment) is not absolutely necessary after liquid cleaning; results just as good as those described above can also be obtained without vapor treatment. It is also possible to replace the steps of treatment of the material, in whole or in part, by steps of treatment with azeotropic preparation in vapor form. Equally good cleaning results were obtained with this procedure as well.

[0071]

Example 2

Defectively printed circuit boards or templates produced in SMD manufacture were treated with a three-component mixture of water, dipropyleneglycolmono-n-propylether or an amine compound or N-heterocyclic compound or organic acids, such as is shown by way of example in Table II. The three-component mixtures used as active cleaning liquids consisted of 90 percent by weight water, 10 - y percent by weight dipropyleneglycolmono-n-propylether, and y percent by weight of one of the compounds listed in Table II. Cleaning was accomplished by the spray process.

[0072]

In order to remove SMD adhesives, the circuit boards or templates were treated at the temperatures indicated in Table II with liquid azeotropic preparations, and the treatment was performed by applying ultrasound (ultrasound is not, however, absolutely necessary for obtaining good cleaning results). The azeotropic preparations were in the form of a milky emulsion which became almost clear when ultrasound was applied. All traces of the adhesives were removed, without the need for providing protective devices in the system, such as explosion prevention devices.

[0073]

The cleaning results were considerably better than those obtained by application of conventional solvents such as butyl acetate or isopropanol. In addition, in the case of the latter two solvents, it is absolutely necessary to provide explosion prevention devices for labor safety reasons.